Using TiO₂ Mesoflower Interlayer in Tubular Porous Titanium Membranes for Enhanced Electrocatalytic Filtration

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ABSTRACT

The current study focuses on synthesis and characterization of novel functionalized anodic membranes for wastewater treatment. This membrane was prepared by first constructing a TiO₂ mesoflower interlayer on a tubular porous titanium membrane and subsequently coating an antimony-doped tin oxide catalytic layer. Physical and electrochemical characterizations of the membranes were evaluated. With TiO₂ mesoflower, the membrane anode obtained a higher oxygen evolution potential, 2.22 V (vs saturated calomel electrode), relative roughness factor (701.7), and electrochemical porosity (99.23%) than membrane anodes without TiO₂ mesoflower. The prepared membrane anode also achieved a low charge-transfer (0.11 Ω) and mass-transfer resistance (0.21 Ω) in filtration mode. The unique features were found linked to its 3-D porous and open structure, and formation of a Ti_{0.2}Sn_{0.8}O₂ solid solution that had a high surface oxygen (O_{ad}) content. The electrocatalytic filtration performance of this membrane was also tested using methyl orange as a model organic pollutant. At a current density of 15 mA cm⁻², the membrane achieved a higher 71.0% removal of methyl orange than 58.0% for the membrane without TiO₂ mesoflower. At a 58.0% removal of methyl orange, the membrane consumed a much lower energy of 0.20 kWh m⁻³ than 5.88 kWh m⁻³ for membrane anodes without TiO₂ mesoflower. The synthesized membrane electrode filter shows promise for future applications aimed to remove organic pollutants from wastewater.

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1. Introduction

Electrocatalytic filtration (EF), a process that takes the advantages of electrochemical oxidation and membrane filtration has drawn much attention recently [1–4]. In the EF process, mass transfer of the target pollutant from the bulk solution to the membrane surface is significantly enhanced due to forced convection by filtration, while the electrochemical oxidation of pollutants that take place simultaneously on conductive membrane anode can be greatly promoted because of the existence of large amounts of active reaction sites on the anode. The EF process shows great promise in future water treatment applications

because of its large treatment capacity, enhanced kinetics and process efficiency at a moderate energy consumption rate.

Many materials have been tested for Electrocatalytic filtration. Among these, carbonaceous materials that include carbon nanotubes (CNTs) [5,6], graphene composite membranes [2] and carbon membranes [1,4] have drawn particular attention because of their high conductivity and low cost. These materials, however, are electrochemically unstable and liable to be oxidized when used as anodes [7]. Tubular porous titanium membranes (TPTM) that are composed of many micron-sized titanium particles have several unique features (e.g. high conductivity, electrochemical stability, three-dimensional (3D) porous structures, flow-through configuration, high surface area, and easy availability [8]), making them particularly suitable for use in EF processes serving as both filtration media and catalyst substrate. In fact, titanium has been extensively used as a supporting material for dimensionally stable anodes [9], and applied in many wastewater treatment processes [10–12].

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Coating electro-catalyst films on membrane filters helps to improve their electrochemical catalytic activity. Among the popular electrochemical catalysts (e.g. boron-doped diamond (BDD) [13], RuO_2 [14], Ti_4O_7 [3,15], IrO_2 [16], PbO_2 [17], and Sb-doped SnO_2 (ATO) [18]), ATO is considered an excellent candidate owing to its high oxygen evolution potential (OEP), 1.8 V (vs saturated calomel electrode, SCE) [18], easy in preparation and cost efficiency. Electrocatalytic properties (e.g. OEP and electrochemical oxidation capacity) of an ATO film are closely related to its physical properties on the substrate, such as its morphology and crystalline structure. Previous reports have demonstrated that introducing a micro/nano-structured interlayer (e.g., aligned TiO_2 nanotubes (NTs) [18–20], Cu nanorods (NR) [21], or TiN nanoparticles (NPs)) [22] between ATO and the titanium substrate is an effective way to significantly increase ATO's OEP and improve its electrochemical oxidation capacity through optimization of ATO's physical properties. These interlayers, however, are not suitable for application in TPTMs as Cu-NRs are inherently electrochemically instable, while the original zero-dimensional structure of TiN-NPs and that of the one-dimensional, stake-shaped TiO_2 -NTs are prone to being destroyed, blocked, or buried post catalyst coating, leading to unexpected loss of the electrode's electrochemically active area and porosity, both of which are vital for EF performance.

The TMF interlayer (TiO_2 mesoflowers) has a unique 3-D, porous, and hierarchical structure with rough morphology. Several studies revealed that the powdered form of TMF exhibited outstanding photo- [23] and electrocatalytic properties [24] in photovoltaic processes [25,26] and photo-catalytic systems for water purification [27]. In our previous investigation [28], TMF nano-arrays have been successfully coated onto an anodic ozone diffuser made of porous titanium, causing the specific surface area of the virgin porous titanium substrate to increase by 200 times. It is speculated that constructing a TMF interlayer on a membrane filter such as TPTM would not only help to increase its catalyst load of ATO by exploiting the unique open structure of TMF, but also improve its electrocatalytic activity, mass transfer properties, and service lifetime. As commercial products of TPTM have been widely used in industrial filtration, drinking water/domestic wastewater treatment [8,29], and the medical applications [30], it is speculated that modifying TPTM-based electrocatalytic membrane electrodes with TMF interlayers would provide a new approach for effective removal of organic pollutants from wastewater in a cost-effective way. As far as we know, no related studies have been reported in the literature.

The objective of this study was to synthesize a novel functionalized anodic membrane electrode TPTM/TMF/ATO that has improved OEP and electrocatalytic oxidation capability and EF performance by introducing the TMF interlayer on TPTMs, which are widely used in many industrial applications. Physical and electrochemical properties of the synthesized electrodes were examined with a focus on their morphology, crystalline structure, electrochemical properties and stability. The EF performance of the synthesized electrodes were also tested using methyl orange (MO) as a model organic pollutant.

2. Materials and Methods

2.1. Materials

TPTMs (purity 99%, 20 mm long with outer and inner diameters of 20 and 10 mm and average pore size of 51 μm) were purchased from Baoji Yinggao Metallic Materials Co., Ltd. (Shannxi, China). Ethanol, concentrated hydrofluoric acid (40 wt.%), and hydrochloric acid (37 wt.%), sodium hydroxide, ethoxyl aminopropyl trisiloxane, tin (II) chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) were purchased from Sinopharm (Shanghai, China). Antimony (III) chloride (SbCl_3) and MO

(methylene orange) were from Sigma-Aldrich. All reagents were of analytical grade and were used without further purification. Milli-Q ultrapure water (Millipore, 18.2 $\text{M}\Omega\text{ cm}$) was used throughout the experiments.

2.2. Preparation of TPTM/TMF/ATO membrane electrodes

Fig. 1 is a schematic illustrating the preparation processes of the TPTM/TMF/ATO Electrode. Briefly, TPTM was first ultrasonically cleaned in acetone, followed by thorough rinsing with 0.3 mol L^{-1} hydrochloric acid and Milli-Q water each for 20 min. Then the TPTM was etched in a mixed acid solution containing hydrofluoric acid and hydrochloric acid at certain concentration for 15 min [28]. The TMF interlayer was then grown *in situ* on the pretreated TPTM via a hydrothermal method detailed in SI. An ATO active layer was subsequently coated on the TMF interlayer by the sol-gel method (SI). Finally, the part was annealed at 500 $^{\circ}\text{C}$ for 1 h to obtain the TPTM/TMF/ATO membrane electrode. To examine the existence of the TMF interlayer on the membrane electrode, ATO-coated TPTMs without the TMF interlayer (i.e., TPTM/ATO) were also prepared following the same procedures except exposing the electrode to the hydrothermal treatment.

2.3. Characterization of synthesized membrane electrodes

The synthesized membranes were characterized with a scanning electron microscope (SEM; INSPECT S50, MAKE FEI, America) at 5 kV from 400 to 70 K magnification, an X-ray diffractometer (XRD, Bruker D8 Advance, Germany, $\text{Cu K}\alpha$ $\lambda = 1.5406 \text{ \AA}$), and an X-ray photoelectron spectroscopy (XPS) spectrometer (Thermo Fisher ESCALAB 250Xi, United Kingdom, $\text{Al K}\alpha$ source). Electrochemical measurements were performed using a conventional three-electrode cell and a CHI 660E electrochemical workstation (CHI, China). A saturated calomel electrode (SCE) and a titanium mesh served as the reference and the counter electrode, respectively. OEP values of the functionalized electrodes were evaluated with linear sweep voltammetry (LSV) performed in 0.1 mol L^{-1} Na_2SO_4 solution at a scan rate of 100 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was conducted in the range of 10^5 Hz to 0.1 Hz at open circuit potential with an amplitude signal of 5 mV, and data were fitted with the ZView software. Cyclic voltammetry (CV) curves were also recorded to examine the voltammetric charge quantity of the electrodes. Tests on accelerated service life were conducted following the procedures reported by Zhao et al. [18]. The amount of coated ATO was determined by weighing the TPTM or TPTM/TMF before and after the ATO coating using a balance with a 0.1 mg [18].

2.4. Electrocatalytic filtration tests and efficacy analysis

Electrocatalytic oxidation efficiency of the synthesized TPTM anodes was examined in an EF system, using MO as a model pollutant. In the EF system, the synthesized anode was surrounded by a titanium mesh cathode with a 2 cm electrode distance. In a typical EF test, the feed was radially suction-filtered through the anode membrane while the permeate was forced out axially from inside of the anode, using a peristaltic pump (Longer Pump BT100). All tests were performed at a fixed flow rate of 3.5 mL min^{-1} under galvanostatic conditions at various current densities. The feed solution contained 50 mg L^{-1} MO (initial pH of 5.9) and 0.1 mol L^{-1} Na_2SO_4 used as supporting electrolyte. Electrochemical degradation of MO was monitored by an UV–vis spectrometer and residual concentration of MO was determined by measuring the absorbance at 464 nm wavelength. The MO removal rate was calculated as $[(C_f - C_p)/C_f]$ where C_f and C_p represent the MO concentration of feed and permeate, respectively. Energy consumption rate E

Fig. 1. Schematic illustration for the preparation of the TPTM/TMF/ATO electrodes.

(kWh m^{-3}) was evaluated using the following equation:

$$E = \frac{10^{-6} \times S \times i \times U}{J} \quad (1)$$

Where S is the anodic nominal geometric surface area (15.7 cm^2), i the applied current density (mA cm^{-2}), U the corresponding cell voltage (V), and J the volume flow rate ($\text{m}^3 \text{ h}^{-1}$).

3. Results and Discussion

3.1. Physical Characterization

3.1.1. SEM analysis

The morphology of catalytic films (e.g. ATO) on a membrane filter electrode has a great impact on its electrochemical properties. The virgin TPTM substrate had a rather smooth surface (Fig. S1), but its surface roughness can be substantially improved by grafting TMF films (Fig. S2) through hydrothermal treatment. Under SEM, the TiO_2 film looks like mesoflowers with pedal thickness measuring $34 \pm 10 \text{ nm}$. It has been reported in an earlier study that coating TMF film on titanium substrate could increase its specific surface area by two orders of magnitude from $0.01\text{--}2.0 \text{ m}^2 \text{ g}^{-1}$ [28]. It is interesting that further coating of ATO catalytic films on the TMF interlayer by the sol-gel method did not destroy the flower pedal's original 3-D structure (Fig. 2a and b). A close examination of the SEM image of TPTM/TMF/ATO (Fig. 2c) indicates that the sol-gel treatment helped deposit many ATO NPs ($85 \pm 25 \text{ nm}$ in diameter) that were uniformly embedded on TiO_2 flower petals, further increasing the surface roughness of TMF. In contrast, TPTM/ATO, the synthesized membrane electrode without hydrothermal treatment before coating the catalytic layer exhibited a much smoother surface (Fig. 2d and e), with much larger ATO grains ($580 \pm 100 \text{ nm}$; Fig. 2f) deposited directly on the titanium substrate. Higher surface roughness observed for TPTM/TMF/ATO

than TPTM/ATO means larger surface area and accordingly higher ATO catalyst load and more active sites favorable for improved electrochemical activities. This is in agreement with measured ATO loading rates for TPTM/TMF/ATO and TPTM/ATO (39 mg g^{-1} TPTM/TMF substrate and 13 mg g^{-1} TPTM substrate, respectively.).

3.1.2. XPS analysis

Fig. 3 shows the XPS spectra of the O 1s bands in the binding energy region of 529–535 eV for TPTM/TMF/ATO and TPTM/ATO. Both spectra can be fitted into two O 1s peaks of O_L (530.0–530.3 eV) [31] and O_{ad} (531.7–532.3 eV) [32] that correspond to the metallic oxides (lattice oxygen of the TMF/ATO nanocomposites) [33] and hydroxides (surface oxygen, such as Sn-OH, Ti-OH and hydrated species) [33], respectively. O_{ad} accounted for 60.89% and 40.78% of the total oxygen for TPTM/TMF/ATO (Fig. 3a) and TPTM/ATO (Fig. 3b), respectively. A higher O_{ad} content for TPTM/TMF/ATO helps the metal oxide (MO_x) catalyst (i.e., ATO) to form active oxygen species with strong oxidation capabilities e.g. physisorbed $\cdot\text{OH}$ (donated as $\text{MO}_x(\cdot\text{OH})$), which are critical for unselective and effective degradation of organic pollutants [18,20,33]. It has been reported that O_{ad} appears to actively participate in electrochemical reactions [34]. In contrast, TPTM/ATO with a lower O_{ad} content tends to form weak oxidants (e.g. chemically absorbed $\cdot\text{OH}$ (MO_{x+1})) on the membrane surface, which are expected to be less effective in degrading organic pollutants [22,24,29].

3.1.3. XRD analysis

Fig. 4 shows the XRD patterns of TPTM/TMF/ATO and TPTM/ATO membrane electrodes. Interestingly, the TPTM/TMF/ATO membrane surface was primarily composed of a ternary metal oxide $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ (JCPDS Card NO: 70-4410); in contrast, TPTM/ATO consisted of mainly pure Ti (JCPDS Card NO: 65-3362) with only small amounts of $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$. This means that TPTM/TMF/ATO

Fig. 2. SEM images of functionalized titanium membrane anodes with different magnifications. Images of TMTP/TMF/ATO (a–c) and TMTP/ATO (d–f).

Fig. 3. XPS spectra of O1s on the surface of TPTM/TMF/ATO (a) and TPTM/ATO (b). The inset shows the content of lattice oxygen species (O_L) and adsorbed hydroxyl oxygen species (O_{ad}) on the surface of the corresponding membranes.

Fig. 4. XRD patterns of TPTM/TMF/ATO (a) and TPTM/ATO (b).

achieved much improved coverage of $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ through introduction of the TMF interlayer, in agreement with morphologies observed in SEM images.

Lattice parameters of the $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ film were calculated from the observed XRD patterns using Bragg's formula [35]. TPTM/TMF/ATO was found to have a more refined $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ lattice structure ($a = b = 4.645 \text{ \AA}$, $c = 2.981 \text{ \AA}$, unit cell volume $V = 64.5 \text{ \AA}^3$) than TPTM/ATO ($a = b = 4.637 \text{ \AA}$, $c = 3.030 \text{ \AA}$, $V = 65.15 \text{ \AA}^3$). The $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ unit cell volume for TPTM/TMF/ATO ($\sim 64.5 \text{ \AA}^3$) was much smaller than that for the standard cassiterite SnO_2 ($71.5 \text{ \AA}^3$) and anatase TiO_2 ($130.4 \text{ \AA}^3$). Larger unit cell volumes ($69.6 \text{ \AA}^3$ – $71.5 \text{ \AA}^3$) have been reported for SnO_2 coated on TiN-NPs [22], TiO_2 -NT [18] and Cu-NR interlayers. These can be explained by the formation of a sosoloid between Sn and Ti through substitution of Sn^{4+} ions (ionic radius $0.83 \text{ \AA}$) in the cassiterite structure with Ti^{4+} ions that has a smaller ionic radius ($0.68 \text{ \AA}$). It is possible that use of the TMF interlayer in TPTM/TMF/ATO would help ATO NPs bind tightly to the underlying Ti substrate by forming the stable $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ sosoloid. Formation of this stable sosoloid would improve the membrane electrode's electrocatalytic oxidation capability, and its electrochemical stability by inhibiting loss of the external ATO catalyst film from the titanium substrate.

3.2. Electrochemical Characterization

3.2.1. Electrochemically active surface area (EASA), roughness factor, and porosity

Electrochemically active surface area, relative roughness factor (R_f), and electrochemical porosity are three other important properties influencing the EF performance of a TPTM membrane. These parameters were determined from CV measurements at different sweep rates in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, following Eqs. S1–S3 (see SI, Fig. S3). Tabulated in Table 1 are the calculated total voltammetric charge (q_T^*), outer voltammetric charge (q_o^*), and inner voltammetric charge (q_i^*) that correspond to total, outer, and inner electroactive surface areas. As shown, TPTM/TMF/ATO had much larger values of q_T^* and q_i^* (833.3 and 826.9 mC cm^{-2} , respectively) than that of TPTM/ATO (71.43 and 53.09 mC cm^{-2}). The calculated electrochemical porosity (q_i^*/q_T^*) for TPTM/TMF/ATO (99.23%) was significantly higher than that of TMF/ATO (74.32%), and the reported ATO electrodes using Cu-NR/ATO (71.15%) and TiN-NP/ATO (61.54%) interlayers. Table 1 also depicts that TPTM/TMF/ATO had a higher R_f of 701.7 than 545.0 for TPTM/ATO, which is in consistent with SEM images observed. These improved electrochemical properties of TPTM/TMF/ATO make it promising to be used in electrocatalytic filtration processes targeting at organic pollutant removal.

3.2.2. Linear polarization curves

Fig. 5 shows the linear polarization curves by linear sweep voltammetry for TPTM/TMF/ATO and TPTM/ATO. The observed OEP for the TPTM/TMF/ATO 2.22 V (vs SCE) was significantly higher than that for TPTM/ATO 1.85 V (vs SCE). This OEP of 2.22 V is also higher than reported OEP of carbon nanotube (CNT) membranes

Fig. 5. Electrochemical characterization of the membrane anodes. Linear sweep voltammetry (LSV) curves and Tafel plots (inset) are shown. The LSV and Tafel experiments were completed at a scan rate of 0.1 V s^{-1} in a $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution.

(1.27 V) [6,7,36], metallic oxide (e.g., TiO_2 , SnO_2 , and Bi-doped SnO_2)-coated carbon-based membranes (1.55–1.89 V) [1,4,7], and Ti_4O_7 membranes (2.14 V) [3]. In addition, TPTM/TMF/ATO also gained a larger Tafel slope of 2.25 V than both TPTM/ATO (0.84 V, inset of Fig. 5) and metallic oxide-coated carbon membranes (1.05–1.37 V) [7]. LSV and Tafel results indicate that introducing TMF between ATO and TPTM can effectively increase membrane's OEP and Tafel slope, which would help to delay onset of oxygen evolution side reactions and an improvement of the organic pollutant degradation efficiency.

3.2.3. Electrochemical impedance

EIS was performed to measure the charge-transfer resistance (R_{ct}) and mass-transfer resistance (W_{mt}) at the membrane electrode/electrolyte interface to better explore the electrochemical and mass transfer properties of TPTM/TMF/ATO and TPTM/ATO membrane electrodes. The R_{ct} , W_{mt} and other EIS data for TPTM/TMF/ATO and TPTM/ATO were calculated using the ZView software via analysis of the EIS curves and proposed equivalent circuits (Fig. S4). As presented in Table 1, the R_{ct} and W_{mt} values for TPTM/TMF/ATO (0.11 and 0.21Ω , respectively) were much lower than that for TPTM/ATO (0.30 and 5.60Ω), suggesting a significant improvement on electron transfer efficiency at the solid-liquid interface due to introduction of the TMF interlayer in the membrane electrode. Further analysis indicate that the lower W_{mt} value for TPTM/TMF/ATO was probably attributed to its thinner diffusion layer L , being only 9% of that for TPTM/ATO (See SI for detailed calculation) [37].

3.2.4. Electrochemical stability

Accelerated service life tests for both synthesized electrodes were conducted to evaluate their electrochemical stability, an

Table 1
The voltammetric charge analyses data (total, outer and inner charge, electrochemical porosity and relative roughness factor) and simulated EIS data of the prepared Ti membranes.

	q_T^* (mC cm^{-2})	q_o^* (mC cm^{-2})	q_i^* (mC cm^{-2})	q_i^*/q_T^* (%)	R_f	R_s (Ω)	C_m (F)	R_m (Ω)	CPE_{dl} (F)	R_{ct} (Ω)	W_{mt} (Ω)	$W-T$ (s)
TPTM/TMF/ATO	833.3	6.40	826.9	99.23	701.67	2.27	0.11	1.70	6.7×10^{-4}	0.11	0.21	0.03
TPTM/ATO	71.43	18.34	53.09	74.32	545.00	2.27	1.19	1.10	6.3×10^{-4}	0.30	5.60	3.68

Note: q_T^* is total voltammetric charge, representing the total electrochemically active surface area of the oxide coating; q_o^* is outer voltammetric charge, representing outer pore electroactive surface area; q_i^* is inner voltammetric charge, representing inner pore electroactive surface area; q_i^*/q_T^* is electrochemical porosity; R_f is relative roughness factor; R_s is the solution resistance; R_m is the membrane resistance; R_{ct} is the charge-transfer resistance; W_{mt} is the mass-transfer resistance; C_m is the membrane capacitance, CPE_{dl} the double-layer capacitance, $W-T$ is an element exponent for finite length diffusion, which is calculated by using ZView software [37].

important property of electrocatalytic membranes, especially for ATO-coated titanium materials. As shown in Fig. 6, although the anodic potential for both TPTM/TMF/ATO and TPTM/ATO increases with electrolysis time, the rate of increase in anodic potential for the former is lower than the later and hence longer accelerated service lifetime (219 min vs 43 min). Calculated actual service lifetime using the proposed empirical relationship (see SI) for TPTM/TMF/ATO was 5 times that of TPTM/ATO (167 vs 33 days), and 1.9 times of the ATO-coated electrode using Cu NR interlayer [21].

The enhanced electrode stability of TPTM/TMF/ATO might stem from the electrode's unique structure through the introduction of the TMF interlayer. First, as the TMF interlayer is formed directly from the TPTM titanium substrate by the hydrothermal method post HF etching, its binding strength with the underlying titanium substrate is expected to be high. Because of the TMF interlayer's large surface area and similar surface properties with ATO, the external ATO coating is expected to have strong adhesion on the mesoflower-structured interlayer, and consequently forming stable $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ sololoid that can substantially slow down the loss of relatively weak catalytic layer of ATO as in the case of TPTM-ATO electrode. For the TPTM-ATO electrode, adhesion strength between titanium and ATO is expected to be low because of their large difference in surface properties.

3.2.5. EF treatment of MO wastewater

The efficacy of the two synthesized anodes for MO removal was tested under varied current densities from 0.1–15 mA cm^{-2} . As illustrated in Fig. 7a, MO removal efficiency by TPTM/TMF/ATO was constantly higher than that by TPTM/ATO, with the highest MO removal rates being 71.0% and 58.0%, respectively, both achieved at 15 mA cm^{-2} . At a fixed MO removal rate, energy consumption for TPTM/TMF/ATO was generally lower than TPTM/ATO (Fig. 7b), with differences in energy consumption observed to increase with higher removal efficiency. For instance, at maximum removal rate of 58.0% by TPTM/ATO, energy consumption by TPTM/TMF/ATO was only 3.4% of that of TPTM/ATO (0.20 vs 5.88 kWh m^{-3}).

The enhanced electrocatalytic degradation of MO by the TPTM/TMF/ATO membrane electrode can be ascribed to its unique physicochemical features, especially the roles played by its TMF interlayer. Having a unique 3D, porous and open structure, this interlayer allows the electrode to have sufficient electrochemical active area (primarily in the form of inner pore area) and hence much lower charge transfer resistance R_{ct} and enhanced electron

Fig. 6. Accelerated service life tests on TPTM/TMF/ATO and TPTM/ATO electrodes in a $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution with an anodic current density of 100 mA cm^{-2} in batch mode (flow rate is zero).

Fig. 7. MO removal efficiency by membrane anodes under different current density. The flow rate is 3.5 mL min^{-1} ; MO concentration is 50 mg L^{-1} ; and a $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution is used as supporting electrolyte (a); Relationship between MO removal efficiency and energy consumption (b).

transfer efficiency in the process of MO degradation on the electrode interface. In addition, the existence of the TMF interlayer promotes to form with the external ATO catalytic layer a strong sololoid of $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ that has a higher O_{ad} concentration, and consequently more physically absorbed $\cdot\text{OH}$ radicals generated by the electrode. Introducing the TMF interlayer also helps to substantially decrease the mass transfer resistance W_{mt} and thus the effective diffusion length travelled by MO molecules inside the TPTM/TMF/ATO membrane electrode, due to remarkably increased electrochemical porosity (99.23%). This improved mass transfer allows fast transport of MO molecules from the bulk solution to reaction sites on TPTM/TMF/ATO. The unique physicochemical properties of the TPTM/TMF/ATO membrane electrode filter shows promises for future applications in efficiently and cost-effectively removing organic pollutants in wastewater.

4. Conclusions

In summary, a novel electrochemical TPTM/TMF/ATO membrane was developed in this study. The electrochemical activity, anode stability, and mass-transfer properties were significantly enhanced as a result of constructing the TMF interlayer via the hydrothermal method and coating with ATO by the sol-gel method. This fabricated membrane TPTM/TMF/ATO has a unique 3-D porous, open structure with high roughness and porosity and

primarily consists of a $\text{Ti}_{0.2}\text{Sn}_{0.8}\text{O}_2$ solid, thus shows superior electrocatalytic (e.g. high OEP value of 2.22 V) and mass transfer properties (e.g. low charge-transfer and mass-transfer resistance). These unique properties consequently results in the significantly enhanced electro-filtration and degradation of MO with a low energy consumption. Overall, these results highlight the advantages of using the electrocatalytic TPTM electrodes in an EF system. The findings also show a great promise for preparing electrocatalytic membrane anodes using common commercial TPTMs as substrate, and for its future application in the efficient and cost-effective water purification.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.08.098>.

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